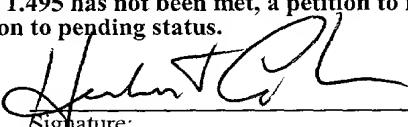


U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV 10-94)		ATTORNEY'S DOCKET NUMBER 109289.00164
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. Unknown 09/674994
INTERNATIONAL APPLICATION NO. PCT/IB99/01266	INTERNATIONAL FILING DATE 13 May 1999	PRIORITY DATE CLAIMED 13 May 1998
TITLE OF INVENTION ORGANIC DYE-IN-POLYMER (DIP) MEDIUM FOR WRITE-ONCE-READ-MANY (WORM) OPTICAL DISCS WITH FLUORESCENT READING		
APPLICANT(S) FOR DO/EO/US Mark Alperovich, Eugene Levich, Irene Zuhl, Svetlana Makievskaya		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 		
Items 11. to 16. below concern document(s) or information included:		
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <ul style="list-style-type: none"> <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: WO 99/59142 Small Entity Declaration 		

U.S. APPLICATION NO. UNKNOWN 09/674994	INTERNATIONAL APPLICATION NO PCT/IB99/01266	ATTORNEY'S DOCKET NO 109289.00164	
17. <input checked="" type="checkbox"/> The following fees are submitted:		CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the EPO or JPO \$840.00			
International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00			
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$970.00			
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$670.00			
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =			
\$ 970.00			
Surcharge of \$130.00 for furnishing the oath or declaration later than <input checked="" type="checkbox"/> 20 months from the earliest claimed priority date (37 CFR 1.492(e)).			
\$ 130.00			
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total Claims	10 - 20 =	0	X \$18.00
Independent Claims	4 - 3 =	1	X \$78.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$260.00
TOTAL OF ABOVE CALCULATIONS =			\$ 1,178.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			\$ 589.00
SUBTOTAL =			\$ 589.00
Processing fee of \$130.00 for furnishing the English translation later than <input checked="" type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+ \$
TOTAL NATIONAL FEE =			\$ 589.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property + \$			
TOTAL FEES ENCLOSED =			\$ 589.00
			Amount to be refunded: \$
			charged: \$
a. <input checked="" type="checkbox"/> A check in the amount of \$ 589.00 to cover the above fees is enclosed.			
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.			
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-2185</u> (109289.00156). A duplicate copy of this sheet is enclosed.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
 Signature: Herbert Cohen _____ NAME _____			
SEND ALL CORRESPONDENCE TO: Customer No.: 002779 BLANK ROME COMISKY & McCUALEY LLP WIGMAN, COHEN, LEITNER & MYERS IP GROUP 900 - 17th Street, N.W. Washington, D.C. 20006			
25,109 / November 9, 2000 Registration No. / Date			

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent application of

Mark ALPEROVICH et al.

Serial No. 09/674,994

Filed: November 9, 2000

For: ORGANIC DYE-IN-POLYMER (DIP) MEDIUM)
FOR WRITE-ONCE-READ-MANY (WORM))
OPTICAL DISKS WITH FLUORESCENT)
READING)

)
Atty. Dkt. No.:
109289.00164



PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the application as follows:

IN THE CLAIMS:

Please amend claims 2-9 as follows:

2. (Amended) DIP medium for the recording layer according to claim [item] 1, wherein said [with the difference that its] fluorescent dye is chosen from xanthene dyes of the eosin and rhodamine groups, acridine, oxazine, azine, perylene, violanthrone, cyanine, phthalocyanine dyes, indigoide colors and porphyrines. [The content of fluorescent dye in the layer is equal to 0, 1-10%.]

3. (Amended) DIP medium for the recording layer according to claim [item] 1, wherein said [with the difference that its] compound generating free radicals is chosen from azo-bisisobutyronitrile, p-bromobenzene diazohydroxide, triphenylmethylazibenzene and diazobenzoyl, nitrosoacetanilide and its derivatives; peroxides such as benzyl peroxide and its derivatives; tert-dibutyl peroxide [, etc]. [The

content of compound, capable to generate free radicals, in the recording layer is equal to 0, 1-20%.]

4. (Amended) DIP medium for the recording layer according to claim [item]1, wherein said [with the difference that the] film-making polymer is chosen from the group of resins consisting of [resins, such as] cellulose esters, [i.e.] including nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers, [i.e.] including methyl cellulose, ethyl cellulose, butyl cellulose, vinyl resins, [i.e.] including polyvinyl acetate, polyvinyl butyral, polyvinyl acetyl, polyvinyl alcohol and polyvinyl [pyrrolidone] pyrrolidone; acrylic resins, [i.e.] including [polymethylmethacrylate] polymethylmethacrylate, polybutyl acrylate, [polymethacrylic] polymethacrylic acid, polyacryl amide polyacrylonitrile.

In claim 5 and Claim 6, line 1, please change "item" to - -claim- -.

7. (Amended) Method of obtaining a single-layer optical WORM disc, comprising the steps of dissolving [which proposes to dissolve] the fluorescent dye, compound and film-forming polymer according to claim 1 [compounds described in item 1] in an organic solvent, chosen from the group consisting of alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents, or to introduce the fluorescent dye, compound and film-forming polymer according to claim 1 [the compounds] into solvent as microcapsules less than [0,2] 0.2 mkm in size, [prepared by known methods,] with a step of covering [future allocation of this] said composition by spin coating, roller coating or dip coating on [the] a substrate, representing a glass, polymethylmethacrylate, polycarbonate or polyethylene terephthalate disc.

8. (Amended) Method of obtaining a single-layer optical WORM disc, comprising [which proposes] creation of a recording layer from two sub-layers, [the] an

lower sub-layer containing fluorescent dye, and [the] a upper sub-layer containing [the] a substance generating free radicals at high temperature.

9. Method of obtaining single-layer optical WORM disc, comprising [which proposes] creation of a recording layer from two sub-layers, [the] an upper sub-layer containing fluorescent dye, and [the] a lower sub-layer containing [the] a substance generating free radicals at high temperature.

Please add new claims 11-12:

-- 11. DIP medium for the recording layer according to claim 2, wherein the content of said fluorescent dye in the recording layer ranges from about 0.1 - 10%.

12. DIP medium for the recording layer according to claim 3, wherein the content of said compound, capable to generate free radicals, in the recording layer ranges from about 0.1 - 20%. --

REMARKS

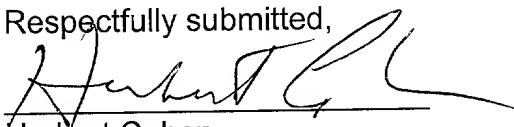
This Preliminary Amendment is submitted to make clarifying revisions to the claims in accordance with U.S. practice and to correct minor typographical errors, which are essentially self-explanatory. No narrowing of the claims scope is intended.

In the event there are any questions relating to this Amendment or to the application in general, it would be appreciated if the Examiner would telephone the undersigned attorney.

Please charge any shortage or credit any overpayment of fees to BLANK ROME COMISKY & MCCUALEY LLP, Deposit Account No. 23-2185 (109289.00164). In the event that a petition for an extension of time is required to be submitted herewith and in the event that a separate petition does not accompany this report, Applicants hereby

petition under 37 C.F.R. §1.136(a) for an extension of time for as many months as are required to render this submission timely. Any fee due is authorized above.

BY:

Respectfully submitted,

Herbert Cohen
Registration No. 25,109

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(202) 530-7400 (phone)
(202) 463-6915 (facsimile)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Alperovich et al.

GAU:

SERIAL NO: Unknown

EXAMINER:

FILED: Concurrently Herewith

FOR: Organic Dye-In-Polymer (DIP) medium for Write-Once-Read-Many (WORM) Optical Discs with Fluorescent Reading

SMALL ENTITY DECLARATION - SMALL BUSINESS CONCERN

I hereby declare that I am:

- The owner of the small business concern identified below;
- An official of the small business concern empowered to act on behalf of the concern identified below:

Name of Concern: TriD Store IP LLCAddress of Concern: Suite 453, 230 Park Avenue, New York, New York 10169

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention described in

- the specification filed herewith;
- the application or patent described above.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below. No rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

- no such person, concern or organization.
- persons, concerns or organizations listed below. (NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities, 37 CFR 1.27)

Full Name	Address	Individual	Small Business Concern	Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate; 37 CFR 1.28(b).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

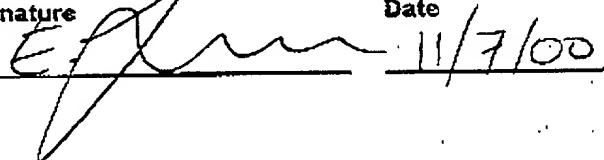
Name

Eugene Levich

Title

President

Signature



Date

11/7/00

ORGANIC DYE-IN-POLYMER (DIP) MEDIUM FOR WRITE-ONCE-READ-MANY
(WORM) OPTICAL DISCS WITH FLUORESCENT READING

Field of the invention

5

This invention is in the field of media for WORM optical discs with fluorescent reading, providing high capacity optical memory, including 3-dimensional optical memory systems.

10 Background of the Invention

Recently WORM optical memory devices have experienced great evolution, providing recording of data with the possibility of its immediate reading. This feature – data recording in a real-time regime – is significant for various applications of optical recording in memory devices, especially for computer systems. For this field duplication of data is not so essential.

20 All WORM optical media of practical interest is based on photothermal principle of recording. The data on such media is recorded by scanning the recording layer with the focused laser beam. The laser power is absorbed by the active medium of the layer and transformed into thermal energy, causing its physical and chemical changes, which can be optically registered at reading.

Photochemical effects can also be used, i.e. optically detected changes in the state 25 of medium, caused by direct interaction of photons with this medium. The efforts are made to use photosensitive medium for photochemical recording on WORM discs. Hence, until now there was no practical application for WORM discs with photon mechanism of recording. The reason can be the non-threshold nature of photochemical recording on the contrary to photothermal recording at the same laser for recording and

reading (with different laser power). Therefore, the photochemical recording can not provide the necessary stability of medium characteristics at multiple reading.

According to the mechanisms of thermally induced effects, the photothermal recording on WORM optical medium with practical applications can be divided in two parts:

- 5 1. Ablative, providing optically registered geometric changes in the thin active layer during its melting, evaporation or chemical transformations, and
- 10 2. With phase change, which does not provide geometric changing of the active layer, otherwise changing its optical constants, that causes optical contrast, which is usually not high for these materials.

Among various types of medium for ablative recording, WORM optical discs with thin (10-100 nm) layers of organic dyes with or without dye-in-polymer are of special interest. Layers of organic dyes provide a range of sufficient advantages in comparison to metal or half-metal layers, used in WORM discs with ablative recording. Advantages are the following:

- 15 • Dyes may have a stronger selective absorption on the recording laser wavelength.
- 20 • Dye layers are more sensitive to the laser radiation because of their small thermal conductivity and low temperature of melting or decomposition. It provides a higher recording capacity.
- 25 • Dye layers provide a higher stability at higher humidity.
- Medium based on dye layers has better signal-to-noise ratio, because of the lack of noise, provided by amorphous layers.
- Coating in the centrifuge makes the layers, that is more simple and cheap than vacuum deposition used for obtaining metal and half-metal layers on WORM discs.

The existing WORM optical discs based on organic dyes has a capacity up to 3.5 GB.

The WORM discs with one recording layer this optical memory capacity is the utmost at least for the diode laser with 780-830 nm wavelength.

Future capacity increase for WORM discs is possible only using three-dimensional optical memory carriers with multilayer data recording and fluorescent reading [A.S. Dvornikov, P.M. Rentzepis, Opt. Comms., v.136, pp. 1-6 (1997); B. Glushko, US Provisional Patent Application, May 8, 1997, N 25457.].

Fluorescent reading offers a range of sufficient advantages in comparison to reading, based on changing the reflection ratio, even in single-layer systems.

One of the advantages is the reduced tolerance for the sizes of recorded pits in comparison to the existing WORM discs. I.e., changing the size on a 100 nm does not influence the reading from fluorescent disc, while it totally eliminates the signal from reflective discs.

Another advantage is the reduced sensitivity of fluorescent discs to changing the slope up to 1 grad that is absolutely intolerable for reflective discs.

Nevertheless, the basic advantage of fluorescent reading is the enhanced capacity of three-dimensional optical memory carriers, realized as multilayer discs.

Use of layers of organic dyes with ablative recording in such medium is not possible owing to the following reasons:

- Reading is realized by laser beam, scanning the change of reflection in the pre-irradiated spots. In a multilayer system, this method causes a strong fall of reading quality, becoming dramatic for systems with over four active layers.
- Heat change of the layer geometrical structure at recording, such as: burning out of holes, creation of bubbles, change of surface texture, etc. It is also unsuitable for

multilayer medium, as it causes dispersion of the reading beam, hence abruptly lowering the level of fluorescent signal.

- The dye concentration in the recording layer of the existing WORM discs is the utmost (up to 99%). In this case, the dye fluorescence is usually suppressed because of high concentration.
5

In the thin dye layers (10-100 nm) of the existing WORM discs the local heating of the medium at recording can reach 700°C. Such high temperature make it difficult to avoid changing the geometrical structure of the layer. Increase of the dye layer thickness
10 up to 200 nm and more using polymer dye at preserving the surface concentration of dye leads to lowering the local heating temperature and allows to prevent the layer deformation. It also provides the appearance and growth of the dye fluorescence due to lowering the concentration suppression effect. However at all the same conditions the layer sensitivity to laser radiation is dramatically lowering, that leads to drop of recording
15 speed and density.

Thus, all the known materials, used for single-layer optical WORM discs with reflective reading, as well as photothermal recording methods can not be used for multilayer optical WORM discs with fluorescent reading. Comparatively thick layers
20 (200 nm and more) of fluorescent dye are likely not suitable for multilayer medium as well without use of special additives and ways of recording, increasing recording speed and density.

Summary of the Invention

25

Considering the above-stated, the purpose of this Invention is the obtaining of a high-sensitive organic dye-in-polymer (DIP) medium for write-once-read-many (WORM) optical discs with fluorescent reading, providing high speed and density of photothermal recording.

The other purpose of the present Invention is the obtaining of a DIP environment with high sensitivity to the recording laser radiation in visual and infra-red range.

5 The future purpose of the present Invention is the obtaining of a DIP environment for single- and multilayer mediums with high optical memory capacity and high signal-to-noise ratio.

10 According to the purpose of the present Invention, the above-stated DIP environment contains a fluorescent dye, capable to absorb the recording laser radiation and to transform the absorbed light power into heat, and a choice of substances, capable to generate free radicals at their decomposition under heating, received from the laser 15 radiation absorption by the fluorescent dye.

According to the other purpose of the present Invention, the above-stated DIP 15 environment contains a fluorescent dye and a non-fluorescent dye, capable to absorb the recording laser radiation and to transform the absorbed light power into heat, and a choice of substances, capable to generate free radicals at their decomposition under heating, received from the laser radiation absorption by the non-fluorescent dye.

20 According to the future purpose of the present Invention, the above-mentioned free radicals cause the discoloring or change of absorption spectrum range of the fluorescent and/or non-fluorescent dyes, thus making the recording.

If the discoloring or change of color of the fluorescent and/or non-fluorescent dyes 25 makes the recording, absorption and fluorescence spectrum ranges of the first dye can just slightly overlap the absorption spectrum of the second dye. In this case, the layer is fluorescent before recording. After recording is made, the irradiated spots lose fluorescence, while the background remains fluorescent.

If the discoloring or change of color of only the non-fluorescent dye makes the recording, than its absorption spectrum range shall overlap the absorption and/or fluorescence spectrum of the fluorescent dye. In this case, the layer is not fluorescent before recording. After recording is made, the irradiated spots become fluorescent, while 5 the background is not fluorescent.

Detailed Description of the Preferred Embodiments

Below there is a detailed description of the mostly preferred ways to reach the 10 intended purposes of the Invention.

First we shall consider the variant when the substrate - a transparent disc from glass, polymethylmethacrylate, polycarbonate or polyethylene terephthalate - is covered with a recording layer, consisting of at least a fluorescent dye, capable to absorb the 15 recording laser radiation, a compound, capable to generate free radicals during decomposition under heating, received from the laser radiation absorption by the fluorescent dye, and a film-forming polymer with high transparency, low heat conductivity and capable to provide the necessary quantum output of the dye fluorescence.

20 Besides, the recording layer can contain compounds, quickening or suppressing photothermal decoloration of the dye, plastifiers, surface-active substances, organic reducers, preventing free radicals oxygen deactivation, etc.

25 The thickness of recording layer can be 100-1000 nm, preferably - 200-500 nm. Fluorescent dye with absorption maximum near the recording laser wavelength is chosen among the xanthene dyes of the eosin and rhodamine groups, acridine, Oxazine, azine, perylene, violanthrone, cyanine, phthelocyanine dyes, indigoide colors and porphyries.

30 The content of fluorescent dye in the layer is equal to 0,1-10%.

The choice of compound, capable to generate free radicals during decomposition under heating, received from the laser radiation absorption by the fluorescent dye, shall consider the relevant temperatures and rate of its decomposition. The possible compounds, capable to generate free radicals, are azo and diazo compounds such as azobisisobutyronitrile, p-bromobenzene diazohydroxide, triphenylmethylazibenzene and diazobenzoyl, nitrosoacetanilide and its derivatives; peroxides such as benzyl peroxide and its derivatives, tert-dibutyl peroxide, etc.

5 The content of compound, capable to generate free radicals, in the recording layer
10 is equal to 0,1-20%.

15 The free radicals, appearing during thermal decomposition of the above-mentioned compounds, are extremely reactive towards organic substances. One of the typical reactions with free radicals is their chain bonding to olefin bond.

20 This reaction is one of the main reasons for decoloration of organic dyes. The free radicals interact with olefin linkages of the dye, making the dye molecules decay, what leads to decoloration or change of color.

25 The film-forming polymer can be selected from a wide range of resins, such as: cellulose esters, i.e. nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers, i.e. methyl cellulose, ethyl cellulose, butyl cellulose; vinyl resins, i.e. polyvinyl acetate, polyvinyl butyral, polyvinyl acetyl, polyvinyl alcohol and polyvinyl pyrrolidone; acrylic resins, i.e. polymethylmethacrylate, polybutyl acrylate, polymethacrylic acid, polyacryl amid polyacrylonitrile.

Film-forming properties of the used resins and the plasticity of the recording layer can be improved by adding to resins the proper plastifier, such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate.

Zinc, lead, or cadmium salts of the higher aliphatic acids and also urea and etanolamine can be used for lowering decomposition temperature of compounds, generating free radicals, and therefore quickening the decoloring process.

5 Hydroquinone, aliphatic and heterocyclic amines, sulfur containing compounds such as thiols, sulfides, disulfides isothiocyanates can be used to slow down decomposition of the compounds, generating free radicals.

Reducing amines can also be added to prevent free radicals oxygen deactivation.
10 They can be n-butylamine, dimethylaminoethyl methacrylate, diethyl-n-butylphosphine, and isoamyl 4-dimethylaminobenzoate.

To create a recording layer of the present Invention, the above-mentioned ingredients are dissolved in organic solvent or introduced in it as microcapsules less than
15 0,2 mkm in size, prepared by known methods, with future covering the substrate with this compound by spin coating, roller coating or dip coating.

The organic solvent is usually selected from alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents. Examples of such
20 solvents include methanol, ethanol, iso-propanol, iso-butanol, tetrafluoro-ethanol, diacetone alcohol, methyl cellosolve, ethyl cellosolve, acetone, methylethylketone, cyclohexanone, N,N-dimethyl-formamide, N,N-dimethylacetamide, dimethylsulfoxide, tetra-hydrofurane, dioxane, ethyl acetate, chloroform, methylene chloride, dichloroethane, toluene, xylene or their mixtures.

25

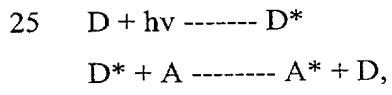
In the other variant of realizing purposes of this Invention the recording layer also contains a non-fluorescent dye with an absorption spectrum range just slightly overlapping the absorption and fluorescence spectrum range of the fluorescent dye and with the maximum absorption value being close to the recording laser wavelength. The
30 layer is fluorescent in its initial state before recording. During recording the non-

fluorescent dye absorbs the laser radiation and transforms the absorbed light power into heat, influencing the generation of free radicals, causing decoloration of the fluorescent dye.

5 (The non-fluorescent dye can also lose color, what does not effect the use features of the medium.) After recording the irradiated spots has no fluorescence, while the background remains fluorescent. The advantage of this variant in comparison to the previous one is that the non-fluorescent dye is more effective in transforming light power to heat, than the fluorescent one, hence in this case we are to use lasers with different
10 wavelength for recording and reading.

In the other variant of realizing purposes of this Invention the recording layer also contains a non-fluorescent dye with an absorption spectrum range covering the absorption and/or fluorescence spectrum range of the fluorescent dye. Concentration of the
15 fluorescent dye shall provide a non-fluorescent layer before recording. Absence of fluorescence in the case, when absorption spectrum range of the non-fluorescent dye overlaps the absorption spectrum range of the fluorescent dye is caused by the fact that absorption optical density of the 1st dye is much higher than the 2nd one.

20 If the non-fluorescent dye absorption spectrum overlaps with the fluorescent dye absorption spectrum, absence of fluorescence is provided by non-radiating intermolecular electronic excitation energy transfer from the second dye D* to the first A upon the Firster's resonance mechanism. This energy transfer process is schematically described by the following equations:



where the * means the electronically excited state.

At recording, the fluorescent and non-fluorescent dyes absorb laser radiation and
30 transform the absorbed light power into heat, which influences the generation of free

radicals, causing decoloration of the non-fluorescent dye. After recording, the irradiated spots become fluorescent. It allows to use the same laser (but with different pulse power) for recording and reading.

5 In the present Invention the single recording layer of the optical disc is either directly deposited on the substrate, or there is also an intermediate layer between the substrate and the recording layer, that improves adhesion and mechanical solidity and lowers heat losses, preventing heat distribution into the substrate. Besides, use of intermediate layer can allow adding into the recording layer the solvents, being aggressive
10 to the substrate.

Besides, the recording layer can consist of two polymer sub-layers, one containing dyes, and the other containing the compound, generating free radicals, with the latter positioned above or below the sub-layer with dyes.

15 The recording layer can be covered with a protective layer or another substrate can be bonded on it to protect the recording layer against the external environment and to improve its safety.

20 For obtaining a multilayer disc for three-dimensional optical memory with fluorescent reading the present Invention proposes consecutive bonding of the described above single-layer discs one to another so that the active recording layers would alternate the inactive separating layers of substrate.

25 For obtaining a multilayer disc the glues shall be used, providing good adhesion of the bonded surfaces and absence of contraction, not influencing negatively the properties of recording layers, not lowering signal-to-noise ratio, transparent for the laser wavelength and fluorescent light. Examples of such glues include UV-hardened optical glues of 3-92, UV-71, UV-69, UV-74, J-91, VTC-2, SK-9 types («Catalog of Summers
30 laboratories»).

Consecutive scanning of every recording layer by a focused laser beam makes the data recording on a multilayer disc. The same way the reading is made.

Example 1.

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To obtain the recording layer medium we prepared the methylene chloride solution, containing as film-forming resin – 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,013% Oxazine 625 Perchlorate with $\lambda_{\text{max. abc.}}$ = 645 nm and $\lambda_{\text{max. fluor.}}$ = 680 nm (Exciton, Inc.) and as a compound generating free radicals – 0,03% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 2.

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To obtain the recording layer medium we prepared the methylene chloride solution, containing as film-forming resin – 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,01% HIDC Iodide with $\lambda_{\text{max. abc.}}$ = 641 nm and $\lambda_{\text{max. fluor.}}$ = 680 nm (Exciton, Inc.) and as a compound generating free radicals – 0,03% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 3.

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To obtain the recording layer medium we prepared the methylene chloride solution, containing 1% polymethylmethacrylate (PMMA), as fluorescent dye – 0,009% HITC Iodide with $\lambda_{\text{max. abc.}}$ = 751 nm and $\lambda_{\text{max. fluor.}}$ = 790 nm (Exciton, Inc.) and as a compound generating free radicals – 0,002% benzyl peroxide. The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 4.

To obtain the recording layer medium the polyvynilacetate (1%), Oxazine 725 Perchlorate (0,013%), plasticizer – dioctyl phthalate (0,2%) and benzyl peroxide (0,03%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 5.

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To obtain the recording layer medium the polyvynilacetate (1%), HIDC Iodide (Exciton, Inc.) (0,01%), dioctyl phthalate (0,2%) and benzyl peroxide (0,003%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

Example 6.

To obtain the recording layer medium the polyvynilacetate (1%), HITC Iodide (Exciton, Inc.) (0,009%), dioctyl phthalate (0,2%) and benzyl peroxide (0,002%) were dissolved in a mixture of ethanol, ethyl cellosolve, iso-propanol, and iso-butanol (4:2:1:1). The compound solvent was filtered, deposited on a glass disc and dried to form a recording layer with 500 nm thickness.

25 Example 7.

The same as in examples 1-6, only benzyl peroxide was not dissolved in the compound for the recording layer, but was introduce in it as microcapsules with average diameter 0,1 mkm.

Example 8.

The same as in examples 1,2,4,5, only the recording layer had two sub-layers. The lower sub-layer of 250 nm thickness contained fluorescent dye, while the upper sub-layer 5 of 250 nm thickness contained benzyl peroxide – as the substance generating free radicals at high temperature. All the other mentioned additives were equally distributed in the two sub-layers.

Example 9.

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The same as in examples 1,2,4,5, only the recording layer had two sub-layers. The lower sub-layer of 250 nm thickness contained benzyl peroxide – as the substance generating free radicals at high temperature, while the upper sub-layer of 250 nm thickness contained fluorescent dye. All the other mentioned additives were equally 15 distributed in the two sub-layers.

Example 10.

The same as in examples 8 and 9, only the sub-layer containing the substance 20 generating free radicals at high temperature, also contained a non-fluorescent dye – Tetraphenyl nickel dithiolene (λ max. abs. = 860 nm). In this case, a diode laser with the 830 nm wavelength made the recording, the reading being made at 650 nm laser wavelength.

Example 11.

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The same as in examples 1,2,4,5,7-9, only the recording layers and the sub-layers, containing fluorescent dyes with the maximum absorption near the laser wavelength 650 nm, also contains the dye – 1,1',3,3,3',3'-hexamethyl-4,5,4'5'-dibenzo-indodicarbocyanine iodide with λ max. Abc. = 685 nm. In this case recording and reading 30 were made with one laser with 650 nm wavelength.

Example 12.

The same as in examples 1-11, only the recording layers and the sub-layers contained azo-bisisobutyronitrile instead of benzyl peroxide.

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Example 13.

For obtaining a multilayer WORM disc 10 single-layer discs, obtained according to one of the examples 1-12, were bonded one after another so that the active recording 10 layers would alternate the inactive separating layers of substrate, using UV-69 glue. The glue was UV-hardened.

Every optical disc obtained according to examples 1-13 was placed on the rotating table, rotated with the speed of 1800 rpm, and recorded by focused pulses of 1 MHz 15 frequency, received from a semiconductor laser with 830 or 650 nm wavelength. The recording power was 30-60 mJ/cm². For comparison, we took a standard CD-R disc by TDK with ablative recording and reflective reading. An optical microscope was used to follow physical and chemical changes of the layer after recording.

20 This discovered decoloration of the dye on the studied examples on the irradiated spots. As a result, on the examples 1-10 and relevant examples 12 and 13 the recorded spots were not fluorescent, while the background remained fluorescent. On the example 11 and relevant examples 12 and 13, the recorded spots were fluorescent, while the background was not. The observation showed no change in the geometrical structure of 25 the recording layer. Under the same conditions, the standard CD-R disc was ablatively recorded by thermoperforation. The signal-to-noise ratio on the studied examples was higher than on the CD-R disc and equal to 4-6.

Thus, the trials under study of the obtained examples have shown their enough 30 sensitivity to the recording laser radiation of visible and infra-red range, high speed and

density of photothermal recording and their suitability for data recording and fluorescent reading on the existing drivers with some small construction changes.

What is claimed is:

1. Dye-in-polymer (DIP) medium for the recording layer of write-once-read-many (WORM) optical disks with fluorescent reading, containing:
 - fluorescent dye, capable to absorb the recording laser radiation;
 - compound, capable to generate free radicals as a result of decomposition under heating, induced by laser radiation absorption by fluorescent dye;
 - film-forming polymer with high transparency, low heat conductivity and providing the necessary quantum output of the dye fluorescence.
2. DIP medium for the recording layer according to item 1, with the difference that its fluorescent dye is chosen from xanthene dyes of the eosin and rhodamine groups, acridine, Oxazine, azine, perylene, violanthrone, cyanine, phthalocyanine dyes, indigoide colors and porphyrines. The content of fluorescent dye in the layer is equal to 0,1-10%.
3. DIP medium for the recording layer according to item 1, with the difference that its compound generating free radicals is chosen from azo-bisisobutyronitrile, p-bromobenzene diazohydroxide, triphenylmethylazibenzene and diazobenzoyl, nitrosoacetanilide and its derivatives; peroxides such as benzyl peroxide and its derivatives, tert-dibutyl peroxide, etc. The content of compound, capable to generate free radicals, in the recording layer is equal to 0,1-20%.
4. DIP medium for the recording layer according to item 1, with the difference that the film-making polymer is chosen from resins, such as cellulose esters, i.e. nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers, i.e. methyl cellulose, ethyl cellulose, butyl cellulose; vinyl resins, i.e. polyvinyl acetate, polyvinyl butyral, polyvinyl acetyl, polyvinyl alcohol and polyvinyl pyrrolidon; acrylic resins, i.e. polymethylmethacrylate, polybutyl acrylate, polymethacrylic acid, polyacryl amid polyacrylonitrile.

5. DIP medium for the recording layer according to item 1, with the difference that the recording layer also contains a non-fluorescent dye with an absorption spectrum range just slightly overlapping with the absorption and fluorescence spectrum ranges of the fluorescent dye and with the maximum absorption value being close to the recording laser wavelength.

6. DIP medium for the recording layer according to item 1, with the difference that the recording layer also contains a non-fluorescent dye with an absorption spectrum range overlapping the absorption and/or fluorescence spectrum range of the fluorescent dye.

7. Method of obtaining a single-layer optical WORM disc, which proposes to dissolve the compounds described in item 1 in an organic solvent, chosen from alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents, or to introduce the compounds into solvent as microcapsules less than 0,2 mkm in size, prepared by known methods, with future allocation of this composition by spin coating, roller coating or dip coating on the substrate, representing a glass, polymethylmethacrylate, polycarbonate or polyethylene terephthalate disc.

8. Method of obtaining a single-layer optical WORM disc, which proposes creation of a recording layer from two sub-layers, the lower sub-layer containing fluorescent dye, and the upper sub-layer containing the substance generating free radicals at high temperature.

9. Method of obtaining a single-layer optical WORM disc, which proposes creation of a recording layer from two sub-layers, the upper sub-layer containing fluorescent dye, and the lower sub-layer containing the substance generating free radicals at high temperature.

10. Method of obtaining a multilayer optical WORM disc by consecutive bonding of the single-layer discs one to another forming a multilayer system with two and more recording layers, in which recording layers alternate separating layers of substrate.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Additional joint inventors are named on separately numbered sheets attached hereto.

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Organic Dye-In Polymer (DIP) Medium for Write-Once-Read-Many (WORM) Optical Discs with Fluorescent Reading
the specification of which

is attached hereto

was filed on November 9, 2000 as United States Application Number or PCT International Application Number 09/674,994 and (if applicable) was amended on _____

I hereby authorize our attorneys to insert the serial number assigned to this application.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 USC §119			
APPLICATION NO.	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
PCT/IB99/01266	PCT	13 May 1999	X

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION(S) UNDER 35 U.S.C. §119(e)	
APPLICATION NUMBER	FILING DATE
60/085,334	13 May 1998

I hereby claim the benefit under 35 U.S.C. §120 of any United States application, or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

PRIOR U.S./PCT INTERNATIONAL APPLICATION(S) DESIGNATED FOR BENEFIT UNDER 35 U.S.C. §120		
APPLICATION NO.	FILING DATE	STATUS — PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: Herbert Cohen, Reg. No. 25,109; Victor M. Wigman, Reg. No. 25,201; George C. Myers, Jr., Reg. No. 27,040; Donald R. Greene, Reg. No. 22,470; Michael C. Greenbaum, Reg. No. 28,419; Charles R. Wolfe, Jr., Reg. No. 28,680; Michael D. White, Reg. No. 32,795; Karl O. Neidert, Reg. No. 39,313; David J. Edmondson, Reg. No. 35,126; Denise C. Lane, Reg. No. 42,780; Peter Weissman, Reg. No. 40,220; Nicholas Bromer, Reg. No. 33,478 and Rafael Perez, Reg. No. 46,041.

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